

Oxidation of Organics Using Tungsten Oxide based Anodes: Fundamental Studies - C. Bock and B. MacDougall (National Research Council Canada)

INTRODUCTION

The use of electrochemical methods for the oxidative removal of organic pollutants from wastewater has attracted much attention (1-3). It has been shown that toxic organic compounds can be removed from aqueous solutions using metal oxide anodes (1). This anodic electrolysis process is carried out at high anodic currents allowing the O₂ evolution reaction (oer) to occur, and is referred to as anodic oxidation in this work. It has been suggested (2) that high concentrations of hydroxy radicals (a presumably intermediate surface product of the oer) is formed at metal oxide anodes that are poor O₂ evolving catalysts. These hydroxy radicals are, in turn, suggested to oxidize the organics present in the electrolysis solution. In another reaction scheme (3), it has been suggested that the pre-adsorption of organics on specific surface sites of the anode is a key factor responsible for increased efficiencies of the anodic oxidation process. However, there is still some controversy about the reaction mechanism of the anodic oxidation of organics. There is also a clear need for the development of stable, non-toxic and economically viable anode materials for this oxidation process.

In this work, the anodic oxidation of aliphatic carboxylic acids and aliphatic alcohols is discussed using tungsten based oxides as novel anode materials.

RESULTS AND DISCUSSIONS

Tungsten oxide (WO_x) based films containing micro-centers of either Pt or Sn were deposited onto Titanium substrates coated with a thin (ca. 150 nm) layer of IrO₂. These oxides were deposited from W-solutions containing also small concentrations of either Pt or Sn-salts, applying constant negative potentials (E's), as has been similarly described elsewhere (4). The tungsten oxides containing Pt and Sn are referred to as Pt/WO_x and Sn/WO_x, respectively. All oxidation studies were carried out using solutions of appropriate organic concentration in 0.5 M H₂SO₄.

Anodic electrolysis studies of tertiary butanol, formic, oxalic and acetic acid were carried out using Pt/WO_x and Sn/WO_x anodes. Initial studies carried out at constant anodic current showed that formic and oxalic acid are quantitatively oxidized to CO₂ using either Pt/WO_x or Sn/WO_x anodes. Neither acetic acid nor t-butanol are oxidized, as indicated by the fact that their concentration remained constant over long electrolysis periods. It has been shown that t-butanol and acetic acid react with •OH generated using UV methods (5). The fact that neither t-butanol nor acetic acid undergo a reaction as a result of the anodic electrolysis using Pt/WO_x or Sn/WO_x anodes could indicate that the •OH surface concentration is small on these particular oxide anodes.

The anodic oxidation reactions of HCOOH and (COOH)₂ were found to exclusively follow 1st order reaction kinetics. This was indicated in the experimentally observed linear relationship between $\ln c_0/\Delta c$ (c_0 being the initial concentration of a particular organic) vs. the electrolysis time passing through zero origin. Therefore, the slope of these plots was used to determine the first order rate constant (k_1). For the same electrolysis conditions, the k_1 value for the (COOH)₂ oxidation was found to be always larger than for the HCOOH oxidation. This is contrary to oxidation studies carried out using •OH generated by the decomposition of

H₂O₂ using UV light. The latter indicated the HCOOH oxidation to be clearly more facile than the (COOH)₂ oxidation. These results suggest the anodic oxidation of HCOOH and/or (COOH)₂ using Pt/WO_x or Sn/WO_x anodes does not solely involve •OH species.

To gain insight into the reaction mechanism for the anodic oxidation of HCOOH and (COOH)₂, constant E electrolysis studies were carried out using Pt/WO_x anodes. The electrolysis solutions were rigorously stirred and the HCOOH and (COOH)₂ oxidation reactions were found to not be mass transport controlled. Current density (J) vs. time plots were obtained over a broad E range as a function of the organic concentration. The influence of increasing organic concentration on the J-time plots was found to be clearly different for HCOOH and (COOH)₂. An increase in the HCOOH concentration was found to significantly decrease the current over a broad E range, thus strongly suggesting that adsorptive interactions between HCOOH and the Pt/WO_x surface are involved in the HCOOH oxidation reaction. Furthermore, k_1 , extracted from experimental HCOOH oxidation data, was seen to increase with more positive E, as would be expected for an electrochemical reaction involving adsorption. Tafel slopes carried out for the HCOOH oxidation to CO₂ further suggested adsorptive interactions of HCOOH with the Pt/WO_x surface.

Contrary to the case of the HCOOH oxidation, an increase in the (COOH)₂ concentration was found to increase the current. The relative increase in the current with the (COOH)₂ concentration vs. the 0.5 M H₂SO₄ solution was found to depend on E and to be large (up to 200 times). The latter indicates that these anodes exhibit high efficiencies for the (COOH)₂ oxidation, consistent with calculated efficiencies for long term (COOH)₂ electrolysis studies. Furthermore, contrary to the case of HCOOH oxidation, the k_1 value for the (COOH)₂ oxidation was found to be independent of E. This indicates that the Tafel slope for the (COOH)₂ oxidation reaction is zero, and hence, could suggest that an initial chemical reaction between (COOH)₂ and the anode surface is the rate determining step in this oxidation reaction.

REFERENCES

- 1.R. Kotz, S. Stucki, and B. Carcer, *J. Appl. Electrochem.*, **21**, 14 (1991)
2. C. Cominellis, *Electrochimica Acta*, **39**, 1857 (1994)
3. J. Feng and D.C. Johnson, *J. Electrochem. Soc.*, **138**, 3328 (1991)
4. P.K. Shen, A.C.C. Tseung, *J. Mater. Chem.*, **2** (11), 1141-1147
5. *Essays on Free-Radical Chemistry*, special Publication 24, the Chemical Society Burlington House, London, 1970.